Honors Chemistry honelectrochemsum06.doc

Redox/Electrochemistry Summary Information

Electrochemistry deals with:

a. using chemical reactions to do work (i.e. provide electricity) (known as **voltaic** or **galvanic** cells).
b. using electricity to force nonspontaneous reactions (known as **electrolytic** cells).

In other words: *The interconversion of chemical and electrical energy through oxidation-reduction*.

Review and Summary of Redox Reactions:
Oxidation:
Gains oxygen
Loses hydrogen
Loses electrons
Reduction:
Loses oxygen
Gains hydrogen
Gains electrons

Oxidation and reduction must occur in pairs. (You can't have an oxidation without a reduction and vice versa)
Charge must be conserved in the chemical reaction.
In a disproportionation reaction, one substance undergoes both oxidation and reduction.

A **reducing agent** is a substance that reduces another substance. It itself is oxidized.
Conversely, an **oxidizing agent** oxidizes another species and is itself reduced.
When referring to an "agent", usually the entire compound is identified, not just the component oxidized or reduced.

Voltaic Cells:

General Idea:
Since redox reactions involve the transfer of electrons from one component of a reaction to another, intercepting that transfer (flow) of electrons, allows useful "work" to be done (i.e. electrical circuits can be powered).

Background:
Recall that **oxidation-reduction** (redox) reactions involve the transfer of electrons from one chemical to another.

Ex. $Mg + Cl_2 \rightarrow MgCl_2$ In this example magnesium loses two electrons and each chlorine gains an electron

$Mg^0 \rightarrow Mg^{2+} + 2e^-$ and is considered oxidized

This is the oxidation half-reaction. It only shows the component oxidized and does not include any spectator ions.

$Cl_2^0 + 2e^- \rightarrow 2Cl^-$ and is considered reduced

This is the reduction half-reaction. It only shows the component reduced and does not include any spectator ions.

The number of electrons lost and gained must always be the same in a redox reaction, so you may need to multiply through each half reaction by a number so that if you add the half reactions back together to get the ***net ionic equation***, the electrons will cancel out.

Things to remember:

Redox reactions always occur in pairs

The charge on any element is zero.

The species being reduced is the oxidizing agent: The species being oxidized is the reducing agent.

Remember the saying: **LEO** goes **GER**

Loses **E**lectrons **O**xidized **G**ains **E**lectrons **R**educed

Question: Determine which element is oxidized and which is reduced in the following reactions:

1. $2AgNO_3 + Cu \rightarrow 2Ag + Cu(NO_3)_2$
2. $F_2 + 2NaCl \rightarrow Cl_2 + 2NaF$

Answers: Silver is reduced ($1^+ \rightarrow 0$), copper is oxidized ($0 \rightarrow 2^+$); Fluorine is reduced ($0 \rightarrow 1^-$), chlorine is oxidized ($1^- \rightarrow 0$).

A more "active" metal will reduce a less active metal (since the more active metal has a greater tendency to lose electrons. Also, in general, most metals will reduce most nonmetals. An **activity series** lists metals from more active to less active as in the following:

Li, K, Ba, Ca, Na, Mg, Al, Zn, Fe, Cd, Ni, Sn, Pb, Cu, Hg, Ag, Au

In other words, lithium is the most active metal in this list and can therefore reduce the ion of any of the metals that come after it in the series. (ex. $3Li + Al^{3+} \rightarrow 3Li^{1+} + Al$)

By separating the oxidation part of a reaction from the reduction part then connecting them by a wire, useful work can be done. As electrons flow from the oxidation side to the reduction side they can pass through a light bulb, motor, etc., providing power to make them run. This type of setup is known as an electrochemical cell (also known as a **voltaic** (or galvanic) **cell**.)

The difference in potential energy between the two sides (relative to hydrogen) is known as the potential difference and is measured in **Volts**. For instance, the reaction between a silver ion and aluminum metal is 2.46V. These values are determined from a list of **standard reduction potentials** that give the relative tendency for an element or ion to be reduced.

The standard hydrogen electrode (SHE) is considered the 0.00V half-cell on the list of standard reduction potentials. All other reactions are measured relative to this electrode.

Reactions with negative reduction potentials are less easily reduced than hydrogen and those with positive values are more easily reduced than hydrogen.

Standard conditions for an electrochemical cell are 1M solutions and 1atm of pressure for gases (usually measured at 25^{o}C).

The standard cell voltage (emf or electromotive force) for an electrochemical cell is

$E^o_{cell} = E^o_{red} + E^o_{ox}$

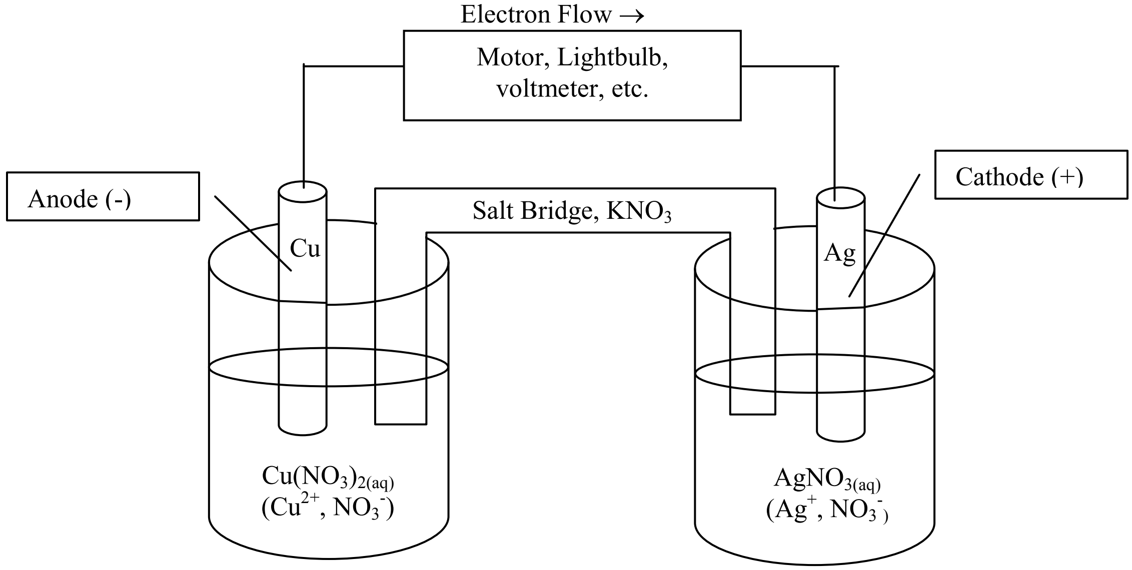
Since values on the standard reduction potential tables are for reductions, the sign of the half-cell voltage must be reversed for E^o_{ox}.

Reactions with more positive values than other reactions on the reduction potential table will always be reduced.

A "spontaneous" reaction will always have a positive cell voltage.

The standard cell voltage for a reduction half reaction is not affected by the coefficients of the equation. Multiplying the equation through by a number will not affect cell voltage.

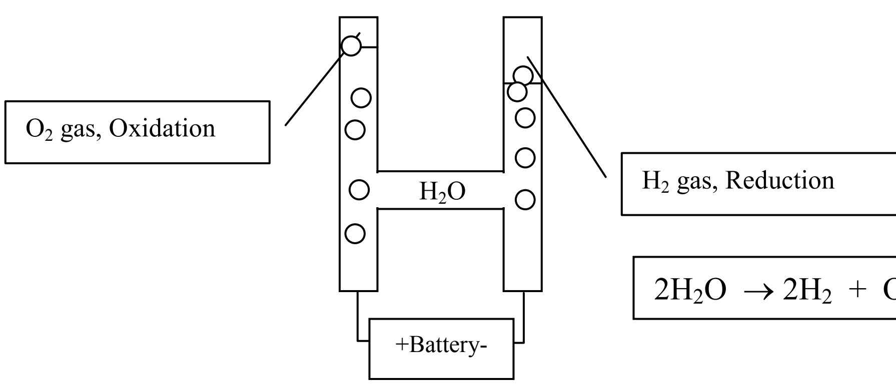
Examine the following diagram of a typical voltaic cell:



Make sure you can define the following:
Anode, Cathode, Site of Oxidation, Site of Reduction, Oxidizing Agent, Reducing Agent, Salt Bridge, Electrode:

Electrolytic Cells: In an electrolytic cell the anode (site of oxidation) is considered the positive electrode and the cathode (site of reduction) is considered the negative electrode.

Electrolytic cells drive nonspontaneous reactions (i.e. in a direction that would not naturally occur). The figure below shows the use of electrical energy to separate water into component hydrogen and oxygen, a reaction that does not occur to any appreciable degree spontaneously.



$$2H_2O \rightarrow 2H_2 + O_2$$

Electrolysis is commonly used for such things as purifying metals, electroplating and reclaiming elements from their compounds. The voltage must be higher than the E^o_{cell} for the reaction in the spontaneous direction.

In electroplating or electrolysis, the **Faraday constant** is often useful. It bridges the relationship between coulombs and moles of electrons. The value is **96,480 C/mol e^-**

Oxidation always occurs at the anode. A good way to remember this is that anode and oxidation both begin with vowels and cathode and reduction both begin with consonants.

In an electrochemical cell the anode is considered negative (-). In an electrolytic cell the anode is considered positive (+).
Example of a typical electrolysis question: An electrolysis experiment is performed to determine the value of the Faraday constant. In this experiment, 28.8g of gold is plated out from a AuCN solution by running an electrolytic cell for two hours with a current of 2.00A. What is the experimental value obtained for the Faraday constant?

Important Things to remember:

1. A **galvanic (voltaic)** cell converts chemical energy to electrical energy through spontaneous reactions. An **electrolytic cell** uses electricity to drive a chemical reaction in a specific direction.
2. A salt bridge in a galvanic cell provides a pathway for ions to travel to keep the overall solutions neutral.
3. **O**xidation **always** occurs at the **A**node whether it is a galvanic cell or electrolytic cell. (Note that they both start with vowels)
4. The anode is considered negative for a galvanic cell and positive for an electrolytic cell.
5. In a cell diagram for a galvanic cell, the anode is listed first.
6. $Cu|Cu^{2+}||Ag^{+}|Ag$ In this cell diagram the solid line separates the electrode from the solutions and the double vertical line represents the salt bridge. Sometimes you may see $Zn|Zn^{2+}||H^{+}|H_2|Pt$ The extra component shows that an inert platinum electrode is passed through a tube of hydrogen gas (i.e. you can't really make an electrode directly out of hydrogen gas, so this method is used).
7. Standard half cell potentials are measure relative to the standard hydrogen electrode (SHE). This half cell is assigned a value of 0V.
8. Reactions with positive half-cell potentials are more easily reduced (gain electrons) than hydrogen ions. Reactions with negative half-cell potentials are less easily reduced (i.e. more easily oxidized).
9. In calculating standard cell voltage $E^o_{cell} = E^o_{red} + E^o_{ox}$, remember that E^o_{ox} is actually $-E^o_{red}$ for that side of the cell reaction (i.e. you have to remember to flip the signs before adding the half cells). Remember, the chart gives "reduction" potentials NOT "oxidation" potentials.
10. The stoichiometry of the cell equation does NOT have any affect on the cell potential (but concentration does!)
11. "Standard" cell conditions are **1M for solutions and 1atm for gases**.
12. Negative cell potentials are nonspontaneous in the direction written and spontaneous in the reverse direction.
13. A ***concentration cell*** is one in which the cell voltage is generated by a difference in molarities of the solutions comprising the two cells. From the rules of equilibrium, even if the metals composing the electrodes are the same, the redox will occur until the molarities of the solutions are balanced. Oxidation will occur at the site of the less concentrated cell.